

III. "On a Law in Chemical Dynamics." By JOHN HALL GLADSTONE, Ph.D., F.R.S., and ALFRED TRIBE, F.C.S. Received May 25, 1871.

(Abstract.)

It is well known that one metal has the power of decomposing the salts of certain other metals, and that the chemical change will proceed until the more powerful metal has entirely taken the place of the other. The authors have investigated what takes place during the process.

The experiments were generally performed as follows:—72 cubic centimetres of an aqueous solution of the salt of known strength, and at 12° Centigrade, were placed in a tall glass; a perfectly clean plate of metal of 3230 square millimetres was weighed and placed vertically in this solution without reaching either to the top or bottom; the action was allowed to proceed quietly for ten minutes, when the plate was removed, and the deposited metal was washed off. The loss of weight gave the amount of metal dissolved, and represented the chemical action.

The most complete series of results was with copper and nitrate of silver.

Nitrate-of-silver solution.		Copper dissolved.		Theoretical.	Difference.
Proportional number.	Percentage of salt.	Actual weights.	Average.		
1.	0.3541	0.0045, 0.0050	0.00475	0.00455	+0.0002
2.	0.7083	0.0135, 0.0140	0.01375	0.01365	+0.0001
3.	1.0623	0.0240, 0.0250	0.0245	0.0259	-0.0014
4.	1.4166	0.0420	0.0420	0.0409	+0.0011
5.	1.7705	0.0600	0.0600	0.0583	+0.0017
6.	2.1246	0.0785	0.0785	0.0790	-0.0005
7.	2.4788	0.0975	0.0975	0.0994	-0.0019
8.	2.8332	0.1230, 0.1230	0.1230	0.1228	+0.0002
9.	3.1873	0.1510, 0.1480	0.1495	0.1481	+0.0014
10.	3.5415	0.1680, 0.1670	0.1675	0.1749	-0.0074
11.	3.8956	0.1955	0.1955	0.2035	-0.0080
12.	4.2497	0.2170, 0.2285, 0.2310, 0.2200	0.2241	0.2336	-0.0095
14.	4.9580	0.2740	0.2740	0.2982	-0.0242
16.	5.6664	0.3270	0.3270		
20.	7.0830	0.4540, 0.4100	0.4320		
24.	8.4994	0.5400	0.5400		
30.	10.624	0.6850	0.6850		
32.	11.333	0.7100	0.7100		
40.	14.166	0.8440, 0.9090	0.8765		
48.	16.999	1.0690	1.0690		
60.	21.246	1.359	1.359		
70.	24.788	1.580	1.580		

In the earlier terms of this series, *twice the percentage of silver-salt gives three times the chemical action.* The close agreement of the observed numbers with those calculated on this supposition as far as the 9th term

is shown in the 5th and 6th columns. The law then breaks down, and after about 7 per cent. the increased action is almost in direct ratio with the increased strength.

The position of the plate in the solution was found to make no difference to this 2-3 law.

Similar series of experiments were made with zinc and chloride of copper, zinc and sulphate of copper, zinc and nitrate of lead, iron and sulphate of copper, and other combinations; and in every instance where the solution was weak and the action simple, the law of three times the chemical change for twice the strength was found to hold good.

It was proved that the breaking down of the law at about 3·5 per cent. of salt in solution was irrespective of the quantity of the liquid, or of the time for which the plate was exposed. With 72 cub. centims. of a 1·41 per cent. solution of nitrate of silver the rate of action remained sensibly the same for as long as twenty-five minutes, notwithstanding the constant deposition of silver. This apparently paradoxical result is due to fresh relays of the original solution being brought up to the plate by the currents produced, and that period of time elapsing before any of the products of decomposition are brought back again in their circuit.

When it was perceived that within easily ascertainable limits the chemical action is the same for similar consecutive periods of time, experiments were made in far weaker solutions. It was only necessary to lengthen the time of exposure. It was thus found that the law of three times the chemical action for twice the strength of solution holds good through at least eleven terms of the powers of 2; in fact, from a solution that could dissolve one gramme of copper during the hour, to a solution that dissolved only 0·000001 gramme, a million times less.

The manner in which the silver is deposited on a copper plate was examined, and the currents produced were studied. At first a light blue current is perceived flowing upwards from the surface of the plate, presently a deep blue current pours downwards, and these two currents in opposite directions continue to form simultaneously. A similar phenomenon was observed in every case where a metallic salt attacked a plate of another metal. The downward current was found to be a solution of almost pure nitrate of copper, containing about three times as much  $\text{NO}_3$  as the original silver solution, while the upward current was a diluted solution of the mixed nitrates. Moreover the heavy current took its rise in the entangled mass of crystals right against the plate, while the light current flowed from the tops of the crystalline branches. It was evident that when the fresh silver was deposited on these branches, and the fresh copper taken up from the plate, there was not merely a transference of the nitric element from one combination to another, but an actual molecular movement of it towards the copper plate, producing an accumulation of nitrate of copper there, and a corresponding loss of salt in the liquid that is drawn within the influence of the branching crystals. Hence the opposite currents.

The amount of action in a circuit of two metals and a saline solution must have as one of its regulating conditions the conducting-power of that solution. It appeared by experiment that a strong solution of nitrate of silver offers less resistance than a weak one; and it was also found, on adding nitrate of potassium to the nitrate of silver, that its power of attacking the copper plate was increased, that the augmentation of the foreign salt increased the action still further, and that the 2-3 law holds good between two solutions in which both the silver and potassium salt are doubled, though it does not hold good if the quantity of foreign salt be kept constant. Similar results were obtained with mixed nitrates of silver and copper.

While these later experiments offer an explanation of the fact that a solution of double the strength produces more than double the chemical action, they do not explain why it should produce exactly three times the effect, or why the ratio should be the same in all substitutions of this nature hitherto tried. The simplicity and wide range of the 2-3 law seem to indicate that it is a very primary one in chemical dynamics.

IV. "On the Organization of the Fossil Plants of the Coal-measures.—Part II. *Lepidodendra and Sigillariæ*." By W. C. WILLIAMSON, F.R.S., Professor of Natural History in Owens College, Manchester. Received June 13, 1871.

(Abstract.)

The *Lepidodendron selaginoides* described by Mr. Binney, and still more recently by Mr. Carruthers, is taken as the standard of comparison for numerous other forms. It consists of a central medullary axis composed of a combination of transversely barred vessels with similarly barred cells; the vessels are arranged without any special linear order. This tissue is closely surrounded by a second and narrower ring, also of barred vessels, but of smaller size, and arranged in vertical laminae which radiate from within outwards. These laminae are separated by short vertical piles of cells, believed to be medullary rays. In the transverse section the intersected mouths of the vessels form radiating lines, and the whole structure is regarded as an early type of an exogenous cylinder; it is from this cylinder alone that the vascular bundles going to the leaves are given off. This woody zone is surrounded by a very thick cortical layer, which is parenchymatous at its inner part, the cells being without definite order; but externally they become prosenchymatous, and are arranged in radiating lines, which latter tendency is observed to manifest itself whenever the bark-cells assume the prosenchymatous type. Outside the bark is an epidermal layer, separated from the rest of the bark by a thin bast-layer of prosenchyma, the cells of which are developed into a tubular and almost vascular form; but the vessels are never barred, being essentially of the fibrous type.